The Early History of Catalysis by Gold

A review of the literature before 1978

Geoffrey Bond

9 Townfield, Rickmansworth WD3 7DD, U.K.
Geoffrey10bond@aol.com

Abstract

Examination of the journal literature and especially patents granted before 1978 reveals frequent observations of the potential of gold as a catalyst, some of which may inspire new directions for work on its applications.

1   Introduction

There is a commonly held belief that the catalytic ability of gold was revealed only in 1987 by the work of Haruta and his co-workers [1], barely anticipated by the studies by myself and my associates on its limited activity for hydrogenation [2] and that of Graham Hutchings and his colleagues on the hydrochlorination of ethyne [3]. It therefore comes as something of a surprise to find that a review of the journal and patent literature undertaken to the end of 1977 contains no fewer than 655 references. This review was conducted by F.H. Lancaster of the Chamber of Mines of South Africa and W.S. Rapson of the International Gold Corporation Ltd; the typescript has kindly been lent to me by Richard Holliday (World Gold Council), and this article is largely based on an analysis of its contents. It only provides the title and reference for each cited work, and a reference to an abstract in either *Gold Bulletin* or *Chemical Abstracts*. What follows is mainly derived from these summaries, those in *Chemical Abstracts* being the more detailed. In the case of patents, a reference to an abstract is also quoted, as well as its number. There are considerably more patents mentioned than papers in journals.

The reader may wonder whether this is a worthwhile exercise, as the science has clearly advanced in leaps and bounds since 1977. For anyone interested in the history of chemistry, the Lancaster-Rapson survey offers an insight into the main preoccupations of catalytic chemists in the 1960s and 1970s. Many of the citations concern attempts to devise better ways for the selective oxidation of hydrocarbons to more valuable products; these cover, for example, the production of oxirane (ethylene oxide) and of vinyl acetate monomer by the Wacker process. Interest was also rapidly developing for catalysts for use in fuel cells. For anyone wanting something new to do, however, a possible benefit in looking back is to seek out ideas that were perhaps prematurely rejected or not developed because the time was not ripe, or because the appropriate form of catalyst had not yet been devised. Some of the reactions noted would repay study from a fundamental standpoint. Many of the citations concern merely a method of catalyst preparation, some of which might merit renewed attention.

Some of the references describe catalysts that contain gold and one or more of the platinum group metals (pgms), especially palladium or platinum. Much of the work of this type was ignored when writing *Catalysis by Gold* [4] on the grounds that in most cases the gold component was inactive, and merely modified the activity of more active pgm. This can be done by limiting the size of the active ensemble of pgm atoms, or less probably by changing their electronic structure, but since gold often seems to have a unique ability as modifier, perhaps because of its relative inactivity, a number of examples of its use in bimetallic systems will be mentioned below. There are however some cases, for example in the selective oxidation of organic molecules and of hydrogen to hydrogen peroxide, where gold plays a more

than trivial modifying role, since combinations of (Au + pgm) are more active than either alone [4].

Work that has been adequately reviewed in recent books [4,5] and review articles [6, 7] is not mentioned again except briefly. The chief purpose of this review is to remind the reader that gold catalysis did not begin in 1987, and that work performed, however inadequately, before then may contain suggestions for the further extension of gold catalysis in the future.

It is necessary to end this Introduction with a word of caution: it is desirable not to accept every claim made in a patent as being the unvarnished truth. For those unfamiliar with the use of patents, the position is briefly thus. A patent application is made to secure priority for an invention, and to obtain the right to practice it exclusively for a limited time. The patent will describe the invention, illustrate it with a number of 'examples' and summarise it in a number of 'claims'. It is often desirable to draft these somewhat more broadly than is strictly necessary, in order to anticipate peripheral areas of application not yet investigated, but which may later turn out to be useful. If however the claims are drawn too broadly and are later found by an opponent to be invalid, the whole patent may be put at risk. It is therefore sensible to view everything claimed in a patent with a degree of suspicion; what is shown as examples is probably true, but since their truth is not part of the process of examination, some degree of caution is always desirable. In this review, information derived from patents is therefore often moderated by words such as 'claimed' to cover this degree of uncertainty.

2 The very early history of gold catalysis

In the period before about 1960, there were a few references to work on the catalytic power of gold; this was always done with macroscopic gold (wire, foil, or powder) and it is therefore not surprising, knowing what we now know, that the measured activities were uniformly dismal. What is however surprising is that none of the hints that this early work provided were followed up and explored for many years. Undoubtedly the earliest observation was that by Dulong and Thenard [8], who in 1823 found that gold was among the metals that catalysed the decomposition of ammonia; this work helped J.J. Berzelius to develop the idea of *catalytic action*. A few years later (1834), Michael Faraday apparently observed that gold catalysed the reaction of hydrogen with oxygen at room temperature [9, 10]. This reaction was studied again in 1906 [11] using gold gauze and involved what must have been the first attempt to follow the kinetics of a catalysed reaction; results relating to the effect of pretreating the gauze in hydrogen at various temperatures are shown in Figure 1. Later, in 1925, it was shown [12] that the positive effect of pre-heating in hydrogen was due to the removal of dissolved oxygen; gold powder was also an effective catalyst [13].
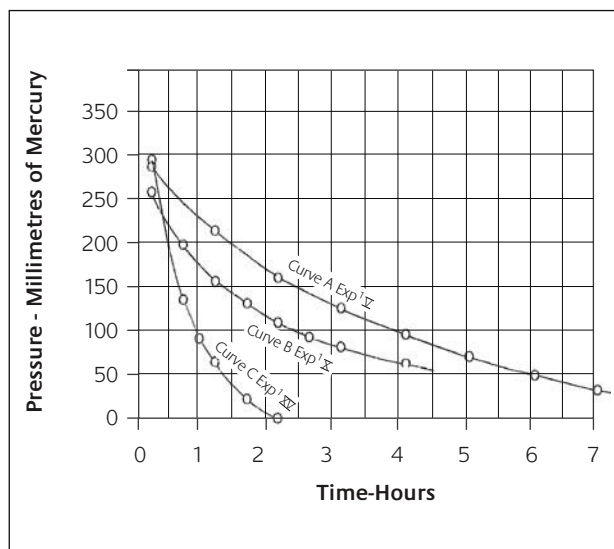
Figure 1 *Reaction of hydrogen with oxygen over gold gauze pretreated in various ways [11]; pressure-time curves at 523 K. Curve A (top), normal condition; Curve B (middle), surface 'hydrogenised' at 523 K; Curve C (bottom), surface 'hydrogenised' at 873 K*

A little later we find the first report [14] of the oxidation of carbon monoxide being catalysed by gold gauze at 573 K, and about this time it was also noted that gold powder had modest activity for ethene hydrogenation at 373 K [15]. It is said that 'Coming events cast their shadows before': this is very true of gold catalysis.

3 Alloys and compounds of gold

Alloys of gold with one or other of the platinum group metals (pgms) have been favourite means of studying the importance of electronic factors in catalysis, and the palladium-gold system has been the most widely used because it forms a continuous range of solid solutions. The first measurements of the effect of gold on the solubility of hydrogen in palladium were made by Thomas Graham in 1861 [16], but his work was criticised in the later study by A.J. Berry [17], who believed Graham's materials were not fully equilibrated. Berry's measurements were in line with all subsequent work.

Almost all preparations of gold catalysts, whether supported or unsupported, start with chloroauric acid (HAuCl$_4$) (Figure 2), despite the fact that chlorine remaining on the catalyst is often a poison. Although ways of removing it have now been developed [4], and halide-free methods such as CVD (chemical vapour deposition) and PCD (physical vapour deposition) are now available, it is of interest to see whether the older literature has any suggestions for other useful alternatives.

Alkyl compounds of gold are unstable, but the formation of a gold-methyl compound was suspected [18] in the reaction of methyl chloride with the AuSi eutectic, which has the lowest melting point (653 K) of any gold alloy; the products comprised CH$_3$SiCl$_3$ and
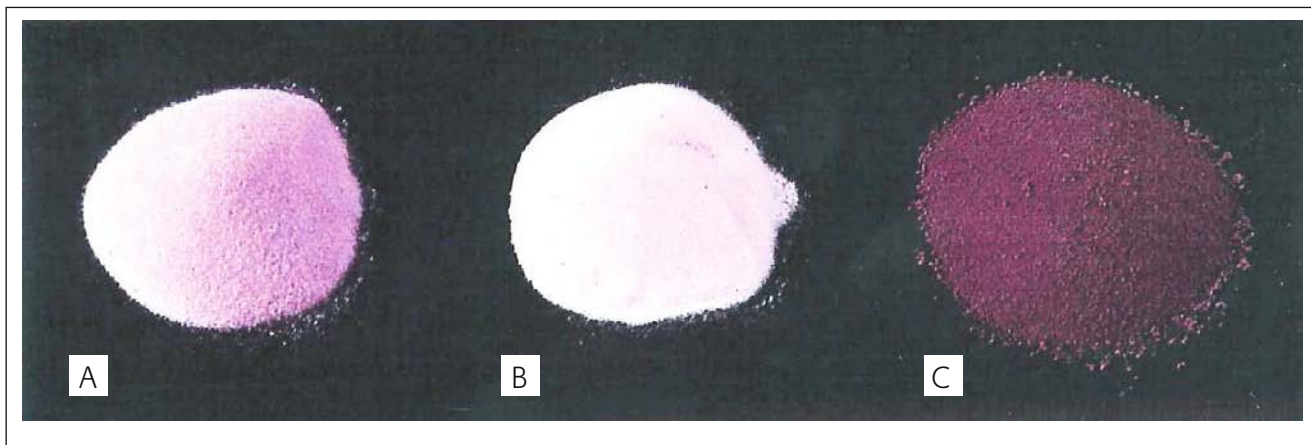
Figure 2 *Brightly coloured products of the reaction of HAuCl$_4$ on SiO$_2$ [2]. A: product obtained after heating precursor containing 0.05% Au in air at 393 K for 48 h; B: the same but with 1.25% Au; C: precursor containing 5% Au reduced in hydrogen at 523 K*

(CH$_3$)$_2$SiCl$_2$ together with a colourless product that condensed on a cold finger, and decomposed to gold and methane above 203 K. It was thought to be Au(CH$_3$)$_3$. Alkyl compounds also containing a halide atom are however much stabler; their preparation and properties were first investigated by Pope and Gibson in 1907 [19], and since this work provides the only mention of these compounds in Greenwood and Earnshaw's text [20] we may assume that no further work was done on them to that date. The colourless (C$_2$H$_5$)AuBr (m.p. 331 K) was made by the Grignard reaction of (C$_2$H$_5$)MgBr and AuBr$_3$; it was soluble in non-polar solvents and chloroform, but not water, and decomposed explosively above 343 K. It could however apparently be stabilised by reaction with ammonia to form white crystals of (C$_2$H$_5$)$_2$AuBr.NH$_3$, which was soluble in a range of solvents, and in dilute HCl, where its solution was stable to boiling. The dark ruby-red (C$_2$H$_5$)AuBr2 was sparingly soluble in organic solvents, but moderately so in warm water; it reacted with ammonia to give a bright yellow powder, but it decomposed violently on heating.

Gold acetate is occasionally used in catalyst preparation, but the compound Au(OH)(CH$_3$COO)$_2$, the making of which has been described [21], has not apparently been tried. On dissolving the residue formed on evaporating a solution of a gold compound with acetic acid in a polar solvent, a non-polar solvent precipitates this compound, which is soluble both in acidic and neutral water and in organic solvents. Greater use of halogen-free compounds of gold is surely to be recommended.

Finally, the shock-sensitive nature of Au-N compounds present when gold salts were reduced with hydroxylamine was noted by Cusumano in 1974 [22]; their hazard has been frequently noted since the accident in the Johnson Matthey laboratories [23], although this has not discouraged the frequent use of ammonia when preparing gold catalysts.
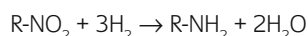
4   Hydrogenation/dehydrogenation

It is not surprising that there are comparatively few references to gold as a hydrogenation catalyst, although there are several mentions of gold as modifying the activity of the platinum group metals (pgms). Thus oxide-supported gold plus a pgm was claimed to catalyse the reduction of maleic acid and of *m*-nitrophenol, as well as 1,3-butadiene and the carbonyl function [12], while the use of (Au + Pt)/SiO$_2$ has been patented for the selective hydrogenation of alkynes and alkadienes [26]; the metals of Group 11 have long been appreciated as effective modifiers of palladium catalysts for these reactions [5]. Early work [15] using gold powder showed it to have mild activity for ethene hydrogenation at 373 K, but the metal showed moderate activity for 1-pentene hydrogenation at 373 K when supported on SiO$_2$ or Al$_2$O$_3$, the first publication appearing in 1973 [2], and this and other later work has been fully reviewed [4,5]. This work provided the first hint that the particle size of the gold might be important, as the turnover frequency began to rise dramatically when the gold content of Au/SiO$_2$ fell below 1 wt % (see Figure 3). It is also active for hydrogenating butadiene and other dienes [4,27]. Its ability to hydrogenate
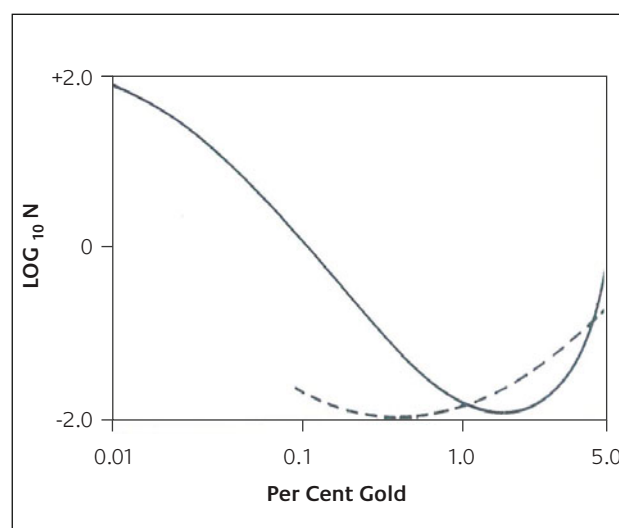
Figure 3 *Dependence of turnover frequency N for the hydrogenation of 1- pentene at 393 K on Au content [2]; full curve, Au/SiO$_2$; broken curve, Au/g Al$_2$O$_3$. N is expressed per total number of gold atoms after 1 h reaction*

the nitro-group has not been widely investigated, but various nitro-compounds have been claimed to be reducible to amines using Au/MnO$_2$ [28], e.g.

$$R\text{-}NO_2 + 3H_2 \rightarrow R\text{-}NH_2 + 2H_2O$$

The use of this support is interesting, as it was employed in some early work on CO oxidation [29], although it has not been widely used since that time.

The dehydrogenation of alkanes and alkyl groups to give C=C bonds is an attractive target reaction, but is not easily achieved on metal catalysts, because of the parasitic reactions that accompany it and cause deactivation. The problem may be avoided in one of two ways: (1) by oxidative dehydrogenation (see Section 6) or (2) tempering the activity of the metal by combining it with an inert component that limits the size of the active ensemble, and thus lowers the formation of toxic intermediates. Thus a patent [30] claims as a dehydrogenation catalyst "a pgm + Re + Sn (II or IV) + a Group 11 metal, especially Au". Materials of similar composition, but without the rhenium, are claimed for dehydrogenating organic compounds in the presence of steam [31], which presumably also helps to control deactivation by carbon deposition. The simple combination of (Pt + Au) has been recommended for dehydrogenating *n*-butane, gold being better than copper as a modifier [31].

5 Reactions involving halogen atoms

One of the more unexpected attributes of gold as a catalyst is its propensity to catalyse reactions involving the halogens and halogenated compounds. The earliest publications are those describing work performed at the University of Birmingham during and immediately after World War II; this was its contribution to the Manhattan Project, and concerned the preparation by fluorination of perfluoro-organic materials, such as might be used in connection with the separation of [235]U from the mixture of naturally-occurring isotopes by gaseous diffusion of UF$_6$. Among the catalysts used for fluorinating a variety of molecules was gold-plated copper turnings [32]; we ought not to scoff at the apparent naivety of such a catalyst, as it might permit the use of high space velocities and short contact times, as well as good thermal conductivity. This programme was under the general direction of Sir Norman Haworth, a carbohydrate chemist, who had won a Nobel Prize for his synthesis of Vitamin C. He is named as one of the inventors of a process for making trifluoroacetic acid by reacting acetone with fluorine over the Au/Cu catalyst at 488 K, collecting the product trifluoroacetic fluoride and hydrolysing it with base to give the acid [33]:

$$CH_3COCH_3 + F_2 \rightarrow CH_3COF + CH_3F$$
$$CH_3COF + H_2O \rightarrow CF_3COOH + HF$$
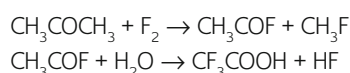
A number of patents dating from the 1960s relate to work on the hydrochlorination of ethene to give a mixture of chloroethene (vinyl chloride) (**I**) and 1,2-dichloroethane (**II**). Thus, for example, a carbon-supported catalyst containing (Au + Cu), together with palladium or zinc at 453 K gave quite high conversions and selectivities to **II** of 80-97% [34]. The metals were converted to their chlorides during reaction, and the presence of sodium chloride was helpful [35]. However, the silica-supported chlorides of (Au + Cu) with an alkali metal chloride at 488 K was claimed to give 78% selectivity to **I**.

It is possible to speculate why gold is often superior to the other Group 11 elements in catalysing reactions of halogenated molecules. It is likely that in many cases an Au^I-HI species is formed on the surface, and by continuation there may arise Au^{III}-HI$_3$ species. In some cases it appears that the process of halogenation oxidises all the metal; oxidation above the +1 or +2 states is not easy with (respectively) silver or copper, and the relatively weak Au-HI bond, together with greater ease of oxidation, may provide the basis for understanding the behaviour of gold. Similar considerations have been used to predict the activity of gold for the hydrochlorination of ethyne, the chemistry of which has been reviewed [4]. More recent work on gold-catalysed reactions of halogenated molecules, including their decomposition, has also been summarised [4].

# 6 Oxidation and oxidative dehydrogenation

An enormous effort has been devoted to attempts to add value to components of hydrocarbon feedstocks by their selective oxidation or dehydrogenation; the latter was covered in Section 4. The various processes can be subdivided as (1) those in which one or more oxygen atoms are added, and (2) those in which hydrogen atoms are removed. In oxidative dehydrogenation, this last process is aided by the presence of oxygen, which by reacting to form water moves the position of equilibrium very much towards the product side, even at moderate temperatures, compared to that obtained in its absence:

$$AH_2 + {}^1\!/_2O_2 \rightarrow A + H_2O$$
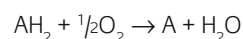
However with both types of process there is the risk of a parallel non-selective oxidation leading to complete degradation of the reactant, and catalysts have to be carefully devised to minimise this. Gold has been shown to have valuable abilities in both sorts of reaction.

A number of patents refer to the use of gold for oxidative dehydrogenation. Ethylpyridines are oxidised to vinylpyridines on 10% Au/Al$_2$O$_3$ spheres [36], while in an interesting anticipation of what later became a well-explored catalyst it was found that ethylbenzene was oxidised to styrene in 50% yield at 973 K using 4% Au/TiO$_2$ (65 m^{2}g^{-1}) as $^1\!/_8$" pellets. At this temperature the gold must have been well and truly

sintered. Other compounds for which gold has been claimed to catalyse oxidative dehydrogenation include ketones [37, 38], esters [39] and acetals [40]; thus for the reaction

$$CH_3CH\,(OCH_3)_2 \rightarrow CH_2 = CH(OCH_3)$$
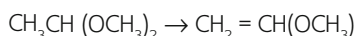
a yield of 99% at 573 K was claimed using a (Pd + Au + KOAc)/SiO$_2$ catalyst. Cyclohexanone can be oxidised to 2-cyclohexenone [41], cyclohexane to benzene [42], and ethylene glycol (1,2-dihydroxy ethane) to glyoxal (OHC-CHO) [43]. Gold may be more active than silver for converting methanol to formaldehyde [44]. These reactions have not in general been re-examined using the latest forms of supported catalysts, nor have they been subjected to detailed kinetic analysis.

Many of the patents granted in the review period concern improvements and extensions to the so-called Wacker reaction:

$$C_2H_4 + HOAc + O_2 \rightarrow H_2C = CH - OAc + H_2O$$
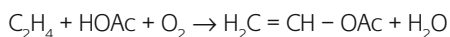
Current industrial processes employ a (Pd + Au + KOAc)/SiO$_2$ catalyst [4]; the patents relate to methods of preparing the catalyst by methods similar to deposition-precipitation [45, 46] or to the use of promoters such as barium compound [47-49] or the sulfate ion [50]. Other claims include the use of Au/SnO$_2$ + a pgm [51], metallic gold by itself [52], and (Cu + Au)/SiO [53]. Catalysts similar to the Wacker type are stated to perform other, possibly related reactions; alkenes having >3 carbon atoms are oxidised to unsaturated carbonyl compounds with a copper-gold alloy (Cu$_{40}$Au$_{2.5}$) [54], while alkyl esters are oxidised in the presence of acetic acid to diacyloxy propenes [55].

$$CH_2 = CH - CH_2 - OAc \rightarrow CH_2 = CH - CH\,(OAc)_2$$
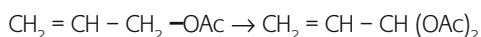
(Ac = -COCH$_3$). In an interesting extension of the Wacker reaction, propene is oxidised to allyl acetate, hydrolysed to the alcohol, and isomerised by (Pd + Au)/SiO$_2$ at 443 K to proprionaldehyde [56]. The reactive methyl group in toluene can also be oxidised, to give benzyl acetate [57]. The Wacker catalyst will also oxidise acetaldehyde to acetic acid at 443 K [58].

Several patents claim that the addition of small amounts of gold (<10%) improves the performance of silver catalysts for the oxidation of ethene to ethene oxide (oxirane) [59-62]. In a quite different mode, Au(PPh$_3$)$_3$Cl in toluene catalyses the oxidation of cyclohexene to a mixture of cyclohexene oxide and cyclohexen-3-one at 313 K in 8% yield [63].

Finally in this section we note several miscellaneous oxidations. In an early (1959) anticipation of Haruta's work, oxygen was removed from a gas stream containing carbon monoxide at 313 K by a catalyst containing (Cu + Fe + Au) made by precipitation from a nitrate solution with Na$_2$CO$_3$; the oxygen level fell below 1 ppm [64]. This is the inverse of the normal application of this reaction. When carbon monoxide is oxidised over gold film, the photocatalysed reaction has a lower activation energy than the dark reaction, due to a 'loosening' of the Au-O bond [65]. The importance of the metal-support junction was also foreseen by comparing the activity of gold microdots in quartz and on NiO, the latter being the more active; similar platinum catalysts were however even more active [66].

Acrolein is oxidised to acrylic acid by mixed oxides containing Au or Ag [67], and crotonaldehyde is dimerised to *p*-tolualdehyde by (Au + Sn + Pb) [68]. Primary alcohols are oxidised to acids by PdAu/Al$_2$O$_3$ [69] and 'sugar alcohols' to aldonic acid [70], foretelling the work of Rossi and others [4], while propene is oxidised to propene oxide by AuBr$_3$ at 453 K and high pressure in a complex brew containing benzene, a nitrite and acetic acid [71]. This process has not been commercialised.

7   Catalysts for fuel cell electrodes

Among the few early patents on this subject that mention gold, two claim the use of a Raney alloy containing silver and gold, besides aluminium [72, 73], one specifically gives the composition as Al$_{79}$Au$_1$Ag$_{19}$ [73]. Another mentions using copper-gold alloys (Cu$_3$Au, CuAu, Cu$_3$Au$_2$) with gallium or aluminium as promoters [74]. Others cite the use of the (Pt + Au) combination: the composition Pt (0.86%) + Au (0.045%) on porous carbon, treated with (NH$_4$)$_2$S solution was used for ethane oxidation [75], while with the same support gold was first deposited and reduced by potassium formate before the inclusion of platinum from H$_2$PtCl$_6$.

8   Other applications of gold catalysts

Two other uses for gold-containing catalysts feature significantly in patents granted in the years before 1978: (i) vehicle exhaust treatment and (ii) hydrocarbon reforming. In the first category, two patents granted to ICI illustrate a supposed role for gold. The first [76] states that NO in exhaust gas is reduced by a catalyst containing cobalt or nickel on an oxide support + some copper + a trace (<1%) of either a pgm or gold or silver + less than 5% chromia. The second [77] is similar, but the promoters named are only copper and gold (<1%). To accomplish the numerous interconnected reactions that can occur in an exhaust treatment reactor it is doubtless necessary to have a multi-component catalyst; recent developments [4] confirm this need.

The term 'hydrocarbon reforming' embraces a number of distinct processes, including skeletal isomerisation (of great importance in petroleum reforming to raise the RON), dealkylation of alkylaromatics (e.g. toluene to benzene), and steam-reforming (as a route to syngas); alkyl groups can also be removed from the aromatic nucleus by steam treatment [78]. A combination of (Re + Au)/high-area alumina is claimed to be a useful petroleum reforming catalyst, giving

a product with an RON greater than 99 [79]. This is scientifically interesting, since rhenium by itself is very active for hydrogenolysis, so we must suppose that gold atoms on the surface of rhenium particles generate small isolated ensembles of the latter, and that these are only capable of isomerisation. This is quite possible, as a similar effect was found with ruthenium catalysts partially poisoned by sulphur [80]. One also recalls the Topsøe work on using gold to moderate the steam-reforming activity of nickel [4]. The Re + Au system should prove rewarding for a fundamental study. In a similar vein, palladium modified by a Group 11 metal on a refractory support (e.g. $(Pd_{0.6}Au_{0.3})\%/Al_2O_3$) has been claimed for petroleum reforming [81].

The moderating influence of the metals of Group 11 was also demonstrated by an ICI patent dated 1966, which claimed a nickel steam-reforming catalyst that also combined one or more pgms plus 10% of a Group 11 metal [82]. This is a clear anticipation of the Topsøe work on the nickel-gold system, where it was shown that gold extended the catalyst life by inhibiting the formation of carbonaceous deposits, through lowering of the mean size of the nickel atom ensembles [4]. Steam-dealkylation of toluene is also effected by gold on alumina (e.g. $0.5\%Au/\gamma$-Al_2O_3) at 973 K [78, 83].

Alkylaromatics have been isomerised by a zeolite (e.g. mordenite) containing zinc and a Group 11 metal [84], and aromatic compounds have been produced from petroleum feedstock by treatment with a catalyst containing Pt + another pgm + a trace of a Group 11 metal (<0.05%) [85]. A supported catalyst having 0.4% Ir + 0.5% Au has been used for the hydrodealkylation of aromatics [86], while various unspecified gold catalysts convert 1,1-dimethylcyclohexane to a mixture of toluene and 1,2-dimethyl-benzene [87]; an $AuNa/Al_2O_3$ isomerises it to 1,2-dimethylcyclohexane, the sodium poisoning the dehydrogenation function [88].

9   Methods for preparing catalysts

Numerous patents describe methods for the preparation of catalysts, usually for some specific application, and many include gold in the list of elements to which the method is supposed to apply. A few of them give methods that appear to have novel or unusual features, and some of them are now briefly described.

A "filamentary gold structure" has been formed by electrodeposition inside the pores of a porous glass [89]; gold has been deposited on FeCr alloy [90], and partial coverage of silver particles by gold has been achieved by electrochemical deposition using $HAuCl_4$ [91]. An unusual if somewhat long-winded way of making 'finely divided catalysts' involves impregnating a support with a metal salt, including a salt of gold, reducing it, and then dissolving away the support [92]; the supports named include silica, alumina, calcium carbonate and ammonium salts, to be dissolved in neutral, acidic or basic water. Various metals including gold are claimed to form salts of the general formula $M(CO_3)(NH_2)_x$ in aqueous

solution and to deposit a basic carbonate onto a support upon heating [93]; calcination and reduction completes the process. Other possible compounds of gold for use in preparing catalysts were mentioned in Section 3.

10   Summary and conclusions

The 20 years that have elapsed since Haruta's discovery [1] of the power of gold catalysts in the oxidation of carbon monoxide, we have slowly got used to the idea that this metal has some proprties at least where it is much superior to the platinum group metals. This contrast may be exemplified by comparing the reported rates of Au/TiO_2 and Pd/SiO_2 catalysts for carbon monoxide oxidation. The former has given a rate of 6.1×10^3 micromol CO s^{-1} g_{Au}^{-1} at 300 K [94], whereas the latter gave less than 2.2×10^{-2} in the same units at 393 K [95]; this tremendous difference highlights the superiority of gold for this reaction, and serves to place this metal firmly in the forefront of catalytic metals. Precise comparison for other reactions is extremely difficult because of the very different temperatures that often need to be used.

This review has only touched on about 75 of the 655 articles and patents listed in the Lancaster-Rapson document, although on close inspection quite a few of the patents only mention gold as a precaution, and do not provide actual examples of its use. Nevertheless, examining the older literature can provide some inspiration for future directions of research, and in particular there are quite a few systems that would bear re-examination, especially by fundamental studies leading to proposals of their mechanisms. It is also quite striking that there are a number of works that provide clear anticipation of the developments that were to follow, especially concerning hydrogenation [24-28], selective oxidation of carbohydrates [69, 70], and oxidation of carbon monoxide [64-66]. As the Bible says: "There is no new thing under the sun. Is there a thing of which it is said "See, this is new"? It has already been in the ages before us" [96].

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